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PATENT & TRADEMARK OFFICE

PATENT
TS0633 (US)
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of JOCHEM VAN DE WEERD Serial No. 10/808,001 Filed March 24, 2004 METHOD OF INCREASING THE CARBON CHAIN LENGTH OF OLEFINIC COMPOUNDS	May 11, 2007

COMMISSIONER FOR PATENTS
P. O. Box 1450
Alexandria, VA 22313-1450

Madam/Sir:

DECLARATION UNDER RULE 131

Dr. ARIE VAN ZON hereby declares:

THAT he is a Principal Research Chemist for Shell Global Solutions International BV; and

THAT he has reviewed WO 03/024910 and understands that this patent application is one of the references used by the Examiner in the office action of March 27, 2007 to reject the claims of the present application; and that the priority date of this reference is September 17, 2001; and

THAT he is familiar with the request for patent action and the report describing the work which was done relating to the present invention; and that the request for patent action and the work referred to above were written and performed in the Netherlands, a WTO country, prior to September 17, 2001; and

THAT the document entitled "Request for Patent Action" enclosed herewith was created prior to September 17, 2001 and describes the invention which is claimed in the present application; and that the document entitled "Dehydration of SHF-Alcohols to Alpha Olefins" was created prior to September 17, 2001; and that this document describes experimental work wherein a primary alcohol, i.e. pure (99%) 1-decanol, and industrially produced primary alcohol mixtures, such as NEODOL-1 (which is largely linear 1-undecanol) or Linevol-911 (a mixture of

C_9, C_{10} and C_{11} 1-alcohols) , made by hydroformylation of a C_{10} olefin or a mixture of C_8, C_9 and C_{10} olefins were subjected to dehydration in a continuous reactor in the gas phase and that 1-decene, 1-undecene or a mixture of 1-nonene, 1-decene and 1-undecene, respectively, were the predominant products; and

THAT the attached documents show that the invention claimed in the present application was made prior to September 17, 2001.

Dr. Arie van Zon further declares that all statements herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date 11th May 2007

Dr. Arie van Zon

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CONFIDENTIAL

LAV/ZEE/CIR/SOC/ES/REP

To be sent to: IP/43
The Hague

REQUEST FOR PATENT ACTION

To be completed by Intellectual Property Division

TS 0633

QA Class(es): 15A05 **Field Code:** CH

Short Title: PROCESS FOR CONVERTING Cx TO C_{x+1} OLEFINS

Date Received:

Attorney: LAVY

To be completed by Reporter

Invention originating from: SRTCA

Department: CTHOC

Research Budget Code(s):

(Code with format *.**.***) 153.151.01**

Brief Description of Research A process for converting a first olefin having x carbon atoms to a second olefin having x+1 carbon atoms, which process comprises:

- a hydroformylation stage wherein the first olefin is reacted with carbon monoxide and hydrogen in the presence of a hydroformylating catalyst to form the corresponding alcohol, followed by
- a dehydration stage wherein the alcohol is dehydrated in the presence of a dehydration catalyst to form the second olefin.

The process is of special importance in the conversion of low-value olefins such as uneven-numbered olefins originating from the Fischer-Tropsch reaction (especially 1-pentene) or from the SHOP oligomerisation (especially iso-nonene) to the corresponding higher-valued even-numbered alpha olefins. Preferred hydroformylation and dehydration catalysts guarantee selectivity towards alpha olefinic end products.

Name(s) of Contributor(s): J. M. van de Weerd

Are there any relevant reports and/or experimental evidence available?
(If YES, please attach copies

NO

Are there any relevant patents or other literature known?
(If YES, please attach details)

Abundant literature about each of the two reactions. Co-SHF is a selective first step and GB-A 2181070 (K605) discloses a selective second step.

Signature of Reporter U. Lavy

Signature of Department Head E P Keffer

Name of Reporter U. Lavy
Extension No.: 2095
Date:

Name of Department Head
E. P. Keffer
CTHCD

From: TABS Editorial Office, CTAIC/2, SRTCA, tel (+31)20 630 2344

Subject: CONF: TABS.

************************** CONFIDENTIAL ***************************

TITLE: Dehydration of SHF-alcohols to alpha olefins

AUTHOR: N. Meijboom (SRTCA-CTHOD/1)

DISTRIBUTION: HET OPC HOD BCH STY PUC SOL RES CAT

KEYWORDS: dehydration, decanol, decene, NEODOL, PAO

INCENTIVE:

Preliminary desk studies have been carried out to evaluate the possibilities of combining a Fischer-Tropsch (FT) unit with a higher olefins and derivatives (HODER) and lower olefins (LO) unit (1). A recent study (1a) is based largely on proven technology and its outcome was promising. The HODER-part of the scheme consists of a series of hydroformylation plants (SHF), which convert (internal) olefins to primary alcohols (NEODOL), followed by a dehydration unit, which converts the primary alcohol to an alpha-olefin. This dehydration step in the FT/SHF units has not been entirely demonstrated and more detailed information is required.

TECHNICAL SCOPE:

We carried out experimental scouting work on the dehydration of 1-decanol, NEODOL-1 and Linevol-911. In collaboration with CTPUC/3

(2) we used an experimental setup designed to the simulate the unit in Moerdijk for MPC (methyl phenyl carbinol) dehydration to styrene. The dehydration was carried out in a continuous reactor in the gas phase (WHSV of 1240 kg.m-3.h-1) using the commercial MPC-dehydration catalyst(aluminium oxide ex-Engelhard, AL-0104- T). Well known side reactions in this chemistry are ether formation, olefin isomerisation and oligomerisation(3). In order to find the optimum dehydration conditions the initial experiments were carried out with pure (99%) 1-decanol, the results of which are summarised in table 1.

Table 1: Dehydration of 1-decanol to 1-decene (based on GLC-Area%)

Temp. (oC)	Conversion (%)	didecyl ether	total decenes	selectivity to 1-decene
282	79.3%	26.7%	51.4%	97.4%
301	87.6%	12.8%	73.6%	96.5%
313	96.2%	1.9%	92.5%	95.0%
325	99.3%	0.2%	97.3%	93.1%

As can be seen in table 1 the best results (high conversion, low ether formation) were obtained at a temperature of 325 oC. At this temperature >99% of the alcohol is converted, the yield of decenes

is 97% and the selectivity to 1-decene is 93%. The two most abundant other decenes were tentatively identified as cis-2-decene (4.1%) and trans-2-decene (1.6%). It may be possible to leave the minor amounts of residual alcohol, ether and isomeric decenes in the product, as they are not expected to hamper the commercially used BF3/ROH catalysed oligomerisation of 1-decene to PAO (Poly Alpha Olefins).

These results led us to apply the same conditions to the dehydration of the SHF-alcohols Neodol-1 and Linevol-911. The dehydration of these alcohols proved to proceed just as smoothly as observed for 1-decanol at 325 oC. Conversion was again some 99% and ether formation as low as 0.2%. We will test the olefins produced from C9-C11 range SHF alcohols for PAO application, because even in todays market situation the price difference between Linevol 911 and 1-decene is such that a low capex transformation like dehydration may be economically feasible from current commercial product (4). The dehydration of Neodol-1 gave a mixture of undecenes with an 1-undecene content of 77.0%. Given the fact that the starting material Neodol-1 contained 83.5% 1-undecanol, the selectivity is comparable (92-93%) to the experiment with 1-decanol. The 2-alkyl branched alcohols (ca. 15-20%) in the Neodol give rise to a different set of alpha-olefins: vinylidene olefins.

Considering the increase in C-number from C10 to C11, the presence of these vinylidene olefins could have a positive effect on PAO-properties. The dehydration of Linevol-911, with a normality (1-alcohol content) of some 82% and containing ca. 19% C9, 45% C10 and 36% C11, gave a mixture of nonenes, decenes and undecenes. The mixture contained about 1% of starting material, 0.5% of ethers, about 15% of 1-nonene, 34% of 1-decene and 27% of 1-undecene. A total of about 76% 1-alkenes (the remainder being predominantly vinylidene olefins) means again a selectivity of 92.5%, as the starting material contained only 82% of 1-alcohols. PAO-production and evaluation, using the above described olefins, will be subject of a future TABS.

In conclusion it can be stated that the dehydration of higher alcohols (C9-C11) to higher olefins proceeds smoothly with the MPC dehydration catalyst in the chosen equipment at 325 oC, showing high conversion (>99%) and a high selectivity to alpha-olefins (>92%). Although at lower temperatures the conversion and ether formation become unfavourable, the selectivity to 1-decene is better (some 97%). A higher conversion at a lower temperature might be obtained with a modified alumina catalyst (5). The planning of further work depends on the results of the performance evaluation of PAO, derived from these olefins and the overall business

attractiveness of the Fischer-Tropsch based HODER-feedstock generator.

REFERENCES:

1. a. H.Donkers, J. Ansorge, M. Cruijsberg, J. van der Sluis; Gas to Chemicals ; CTBCH/2629/97 b. A. van Zon, H.J. van Milligen and A.K. van Helden; Review of the options for a HODER feedstock generator ; PRC/0369/95 c. M.I. Barr, Cracking of Bintulu paraffins , SICM-CMFP/212 Note of 11 March 1993

2. Data can be retrieved from lab notebook PRC/LJ008/95, NM1464-69

Equipment was kindly made available to us by S.H. Johnson and J.C. van Roermund. The practical assistance of M. van Zwienen is gratefully acknowledged.

3. R. Askani in Houben-Weyl, Methoden der Organischen Chemie, Band V/1B, vierte auflage, 45-62; Eugen Moeller Toebingen (1972)

4. Communication with S.R. Brown (CED/11) d.d. 6-6-1997 5. Zinc aluminates are known dehydration catalysts that work at a lower temperature (e.g. C.S. John; Shell patent GB2181070A)

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